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SPECIFICATION

HEAT-RESISTANT, AUSTENITIC, SPHEROIDAL GRAPHITE CAST IRON

FIELD OF THE INVENTION

5 [0001]

The present invention relates to a heat-resistant, austenitic spheroidal graphite cast iron suitable for exhaust equipment members, etc. for automobile engines, such as turbocharger housings, exhaust manifolds, catalyst cases, etc.

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BACKGROUND OF THE INVENTION

[0002]

Exhaust equipment members for automobile engines, such as turbocharger housings, exhaust manifolds, catalyst cases, exhaust manifolds integrally cast with turbocharger housings, exhaust manifolds integrally cast with catalyst cases, etc. are required to have high heat resistance such as oxidation resistance, high-temperature yield strength, thermal fatigue life (thermal cracking life), etc., because they are used under high-temperature, severe conditions of being repeatedly exposed to a high-temperature exhaust gas passing therethrough, and because they are exposed to sulfur oxides, nitrogen oxides, etc. in the exhaust gas. Accordingly, the exhaust equipment members for automobile engines have conventionally been formed by heat-resistant cast iron such as austenitic spheroidal graphite cast iron (called "NI-RESIST") having high heat resistance, ferritic or austenitic cast stainless steel containing large amounts of elements such as Ni, Cr, W, etc. for improved heat resistance, etc.

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20

25 [0003]

A typical austenitic spheroidal graphite cast iron is FCDA-NiSiCr 35 5 2 (JIS G 5510) having a composition comprising, by weight, 2.0% or less of

C, 4.0-6.0% of Si, 0.5-1.5% of Mn, 34.0-36.0% of Ni, and 1.5-2.5% of Cr, which has elongation of 10% or more and 0.2-% yield strength of 200 N/mm² or more at room temperature. However, despite good elongation and yield strength at room temperature, good castability, and relatively good
5 high-temperature yield strength at an exhaust gas temperature of lower than 900°C, this austenitic spheroidal graphite cast iron has insufficient oxidation resistance and thermal fatigue life, because oxide films, from which cracking occurs, are formed at temperatures of 900°C or higher. Therefore, the austenitic spheroidal graphite cast iron cannot be used for exhaust equipment
10 members exposed to a high-temperature exhaust gas at 900°C or higher.
[0004]

JP59-113160A discloses austenitic spheroidal graphite cast iron having a composition comprising, by weight, 2.5-3.5% of C, 1.5-3% of Si, 0.2-8.0% of Mn, 1-3% of Cr, 18-35% of Ni, 0.05% or less of P, and 0.15% or
15 less of S, the balance being Fe and impurities, which has excellent thermal cracking resistance. It describes in Examples that with a composition comprising 2.9% of C, 2.7% of Si, 1.5% of Mn, 2.0% of Cr and 25.0% of Ni, the balance being Fe and impurities, no cracking occurred at all in a 300-hour durability test at exhaust gas temperatures between 850°C and 200°C.
20 Though this austenitic spheroidal graphite cast iron is provided with improved thermal cracking resistance by reducing the amounts of harmful precipitates in a microstructure by reducing the amount of Si, it does not have sufficient ductility (room-temperature elongation) to resist tensile stress at room temperature.
25 [0005]

JP63-114938A discloses a heat-resistant cast iron having a composition comprising, by weight, 2.5-3% of C, 2.6-3.2% of Si, 0.6-1.0% of Mn, 1.8-5.0% of Cr, 16.0-30.0% of Ni, 0.08% or less of P, 0.02% or less of S,

0.03-0.10% of Mg, 0.8-3.3% of Nb, and 0.18-0.7% of Ce and/or La, the balance being Fe and inevitable impurities, which exhibits excellent oxidation resistance particularly in an environment of repeated heating and cooling. In this heat-resistant cast iron, the precipitation of inevitable impurities such as P, S, etc. in grain boundaries are suppressed by the addition of Nb to strengthen the grain boundaries and prevent their corrosion, and oxide films are made denser and stronger by the addition of Ce and/or La to improve oxidation resistance. However, it does not have sufficient strength (high-temperature yield strength) to resist compression stress applied to the constrained exhaust equipment members at high temperatures.

[0006]

JP06-128682A discloses a high-heat resistance cast iron having a composition comprising 13.0-40.0% by weight of Ni and 3.0-10.0% by weight of Si, the balance being substantially Fe, and at least one element selected from the group consisting of Nb, Mo, V, Ti and Ta being 5-30% by weight of Si, which suffers small weight loss by oxidation. It describes in Example a composition comprising 2.83% by weight of C, 6.17% by weight of Si, 0.85% by weight of Mn, 0.056% by weight of Mg, 20.3% by weight of Ni, 1.99% by weight of Cr, and 1.6% by weight of Mo. This heat-resistant cast iron has improved heat resistance and high-temperature fatigue strength, because it contains as much Si as 3.0-10.0% by weight, Mo being 5-30% by weight of Si. However, this cast iron has toughness reduced by the addition of a large amount of Si. In addition, the mere addition of Mo hinders the spheroidization of graphite and increases the number of carbides, particularly resulting in insufficient ductility at room temperature.

[0007]

JP07-6032B discloses flake graphite cast iron for cylinder heads having a composition comprising, by weight, 3.2-3.7% of C, 2.0-2.4% of Si,

0.2-0.8% of Mn, 0.1% or less of P, 0.1% or less of S, 0.1-0.4% of Cr, 0.2-0.6% of Ni, 0.3-0.6% of Mo, and 0.02-0.05% of Sb, the balance being Fe, which has a thermal fatigue resistance particularly improved by Sb.

However, this cast iron has insufficient room-temperature elongation,

- 5 high-temperature yield strength and thermal fatigue life because of no spheroidization of graphite, particularly insufficient heat resistance when exposed to a high-temperature exhaust gas at 900°C or higher.

[0008]

- 10 Recently, further reduction of an exhaust gas and improvement in fuel efficiency are increasingly demanded for the purpose of maintaining global environment. Thus, progress has been achieved in increase in the power of engines and combustion temperatures, resulting in increase in the temperature of an exhaust gas passing through exhaust equipment members for automobile engines.

15 [0009]

In most automobile engines, gasoline is mixed with air in an intake manifold or a collector as an air-intake member and then supplied to a combustion chamber of the engine. In this structure, if gasoline leaks from the air-intake members by the collision of an automobile, it may be ignited.

- 20 To prevent such an accident, the air-intake members are conventionally connected to the engine on the rear side, while exhaust equipment members such as an exhaust manifold and a turbine housing are connected to the engine on the front side. However, because of increase in the power of engines and combustion temperatures, so-called direct-injection engines having
- 25 combustion chambers into which gasoline is directly injected have recently been widely spreading. In the direct-injection engine, because gasoline is directly introduced into a combustion chamber from a fuel tank, only the slightest amount of gasoline would leak if the automobile collided, resulting

in little likelihood that the collision leads to a large accident. Accordingly, arrangement has been being adopted such that the air-intake members are disposed in front of the engine, while the exhaust equipment members are disposed on the rear side of the engine.

5 [0010]

Further, in some cases, exhaust equipment members are disposed on the rear side of an engine, so that they are directly connected to an exhaust gas-purifying apparatus to suppress the decrease of an exhaust gas temperature at the time of starting the engine, thereby improving the initial performance of an exhaust gas-purifying catalyst. However, when the exhaust equipment members are disposed on the rear side of the engine, the surface temperatures of the exhaust equipment members are excessively elevated because the exhaust equipment members are less likely to be brought into contact with the wind during the driving of an automobile. In addition, the exhaust equipment members for automobile engines are exposed to sulfur oxides, nitrogen oxides, etc. contained in the exhaust gas.

15 [0011]

Thus, the exhaust equipment members for automobile engines are not only required to have high oxidation resistance, but also should withstand severer conditions than conventional ones, such as elevated exhaust gas temperatures, elevated surface temperatures because of rear arrangement, etc.

20 [0012]

Specifically, the exhaust equipment members are exposed to as high an exhaust gas as 900°C or higher, particularly around 1000°C, so that they are required to have higher heat resistance. The high or excellent heat resistance means that even when the exhaust equipment members are exposed to a high-temperature exhaust gas containing sulfur oxides, nitrogen oxides, etc., oxide films, from which cracking occurs, are less likely to be formed

(excellent oxidation resistance), that the exhaust equipment members are strong enough to resist a compression stress generated when the constrained exhaust equipment members are subjected to high temperatures (high yield strength at high temperatures), and that the exhaust equipment members more
5 desirably withstand many cycles of operation and stop until thermal fatigue fracture occurs by cracking (long thermal fatigue life).

[0013]

The exhaust equipment members are required to have excellent heat resistance and ductility. Vibration and shock are applied to the exhaust
10 equipment members in a production step and an assembling step to an engine, at the time of starting an automobile, during its driving, etc. Thus, the exhaust equipment members are required to have sufficient ductility to resist tensile stress generated by the vibration and shock, so that no cracking occurs. Because metals have low toughness at low temperatures, ductility at room
15 temperature or lower is particularly important. The ductility at room temperature or lower is generally expressed by room-temperature elongation.

[0014]

It was proposed to use ferritic or austenitic cast stainless steels withstanding higher temperatures for exhaust equipment members, etc., in
20 place of heat-resistant cast irons such as austenitic spheroidal graphite cast iron. However, these cast stainless steels are expensive because elements such as Ni, Cr, W, etc. are contained, though they have excellent heat resistance and high-temperature strength.

[0015]

25 These cast stainless steels are also poor in castability because of lower C contents and higher melting points than those of the austenitic spheroidal graphite cast iron. Accordingly, when cast stainless steel is used to form thin exhaust equipment members with complicated shapes, they are

inevitably expensive because of high material and production costs.

OBJECTS OF THE INVENTION

[0016]

5 Accordingly, an object of the present invention is to provide an
inexpensively producible, heat-resistant, austenitic spheroidal graphite cast
iron, whose heat resistance such as oxidation resistance, high-temperature
yield strength, thermal fatigue life, etc. when exposed to an exhaust gas at
900°C or higher is improved without deteriorating room-temperature
10 elongation.

DISCLOSURE OF THE INVENTION

[0017]

As a result of intense research on improving the oxidation resistance,
15 high-temperature yield strength and thermal fatigue life of austenitic
spheroidal graphite cast iron at 900°C or higher, particularly around 1000°C
without deteriorating room-temperature elongation, the following has been
found: (a) the addition of a proper amount of Mo having little tendency to
hinder the spheroidization of graphite despite its nature as a carbide-forming
20 element provides precipitation strengthening to a cast matrix structure,
thereby providing the austenitic spheroidal graphite cast iron with improved
high-temperature yield strength and a small average thermal expansion
coefficient in a range up to near 1000°C, a small thermal strain in a
high-temperature range, which is determined by the product of the thermal
25 expansion coefficient and a temperature, and thus small thermal stress; (b) the
synergistic effect of Si, Cr and Mo makes a passive film formed on a surface
denser and stronger, thereby suppressing surface oxidation and increasing a
thermal fatigue life; and (c) the addition of proper amounts of Sn and/or Sb

keeps a graphite spheroidization ratio at 75% or more, thereby securing enough room-temperature elongation and preventing the disappearance of graphite by internal oxidation. The present invention has been completed based on these findings.

5 [0018]

Thus, the heat-resistant, austenitic spheroidal graphite cast iron of the present invention comprises 1-4.5% by weight of Mo, and 0.001-0.5% by weight of Sn and/or Sb being as (2Sn + Sb).

[0019]

10 In a preferred embodiment of the present invention, the heat-resistant, austenitic spheroidal graphite cast iron has a composition comprising 1-3.5% of C, 1-6.5% of Si, 3% or less of Cr, 10-40% of Ni, 1-4.5% of Mo, 0.001-0.5% of Sn and/or Sb as (2Sn + Sb), and 0.1% or less of a graphite-spheroidizing element, on a weight basis. The heat-resistant,
15 austenitic spheroidal graphite cast iron of the present invention preferably further comprises 0.3% or less by weight of N.

[0020]

The above heat-resistant, austenitic spheroidal graphite cast iron preferably has room-temperature elongation of 2% or more, weight loss by
20 oxidation of 30 mg/cm² or less when kept at 950°C for 200 hours in the air, and 0.2-% yield strength of 55 N/mm² or more at 950°C in the air. It also preferably has a thermal fatigue life of 400 cycles or more in a thermal fatigue test of heating and cooling at the highest temperature of 950°C, a temperature amplitude of 800°C and a constraint ratio of 0.5. It further preferably has an
25 average thermal expansion coefficient of $18 \times 10^{-6}/^{\circ}\text{C}$ or less in a range from room temperature to 1000°C.

BRIEF DESCRIPTION OF THE DRAWINGS

[0021]

Fig. 1 is a photomicrograph (magnification: 100 times) showing the microstructure of the heat-resistant, austenitic spheroidal graphite cast iron of Example 12.

5 Fig. 2 is a photomicrograph (magnification: 100 times) showing the microstructure of the heat-resistant, austenitic spheroidal graphite cast iron of Comparative Example 9.

Fig. 3 is a graph showing the relation between a graphite spheroidization ratio and room-temperature elongation in the heat-resistant,
10 austenitic spheroidal graphite cast iron.

Fig. 4 is a graph showing the relation between a Mo content and room-temperature elongation in the heat-resistant, austenitic spheroidal graphite cast iron.

Fig. 5 is a graph showing the relation between a Mo content and weight loss by oxidation in the heat-resistant, austenitic spheroidal graphite
15 cast iron.

Fig. 6 is a photomicrograph (magnification: 400 times) showing the microstructure of the heat-resistant, austenitic spheroidal graphite cast iron of Example 12 after the oxidation test.

20 Fig. 7 is a photomicrograph (magnification: 400 times) showing the microstructure of the heat-resistant, austenitic spheroidal graphite cast iron of Comparative Example 4 after the oxidation test.

Fig. 8 is a graph showing the relation between a Mo content and high-temperature yield strength in the heat-resistant, austenitic spheroidal
25 graphite cast iron.

Fig. 9 is a graph showing the relation between a Mo content and a thermal fatigue life in the heat-resistant, austenitic spheroidal graphite cast iron.

Fig. 10 is a perspective view showing an exhaust part comprising an exhaust manifold, a turbocharger housing and a catalyst case.

Fig. 11 is a side view showing an example of turbocharger housings.

Fig. 12 is a cross-sectional view taken along the line A-A in Fig. 11.

5 Fig. 13 is a perspective view showing the appearance of a turbocharger housing formed by the heat-resistant, austenitic spheroidal graphite cast iron of Example 12 near a waist gate after a durability test of 1000 cycles.

10 Fig. 14 is a perspective view showing the appearance of a turbocharger housing formed by the heat-resistant, austenitic spheroidal graphite cast iron of Comparative Example 4 near a waist gate after a durability test of 540 cycles.

DESCRIPTION OF THE PREFERRED EMBODIMENTS

15 [0022]

The present invention will be explained in more detail referring to embodiments below without intention of restricting the present invention thereto.

[0023]

20 [1] Composition of heat-resistant, austenitic spheroidal graphite cast iron

The composition and properties of the heat-resistant, austenitic spheroidal graphite cast iron of the present invention will be explained in detail below. The percentage is expressed on a weight basis unless otherwise mentioned.

25 [0024]

(1) C (carbon): 1-3.5%

C is an element for crystallizing graphite and improving the flowability of a melt. When C is less than 1.0%, spheroidal graphite cannot

be crystallized, and the melt has too low flowability. On the other hand, when C exceeds 3.5%, coarse graphite particles are formed, resulting in spheroidal graphite cast iron with poor room-temperature elongation, and shrinkage cavities are likely to be formed during casting. Accordingly, C is

5 1-3.5%, preferably 1.5-2.5%.

[0025]

(2) Si (silicon): 1-6.5%

Si is an element contributing to the crystallization of graphite. The inclusion of 1% or more of Si leads to the formation of a passive film of

10 silicon oxide near a surface, resulting in spheroidal graphite cast iron with improved oxidation resistance. On the other hand, Si exceeding 6.5% provides a hard matrix, resulting in remarkable decrease in room-temperature elongation and the deterioration of machinability. Accordingly, Si is 1-6.5%, preferably 4.5-6%.

15 [0026]

(3) Cr (chromium): 3% or less

Cr is combined with carbon to precipitate carbides in a cast iron matrix, thereby improving the high-temperature yield strength of the spheroidal graphite cast iron by precipitation strengthening of the matrix. It

20 also forms a dense passive film of chromium oxides near a surface, thereby improving oxidation resistance. However, Cr exceeding 3% deteriorates workability and adversely affects the spheroidization of graphite. Accordingly, Cr is 3% or less, preferably 1-3%.

[0027]

25 (4) Ni (nickel): 10-40%

Ni is an important element to austenitize the matrix structure. When Ni is less than 10%, an austenite is not sufficiently stabilized. On the other hand, when Ni exceeds 40%, an austenitizing effect is saturated, resulting in

only increase in a material cost. Accordingly, Ni is 10-40%, preferably 25-40%. The more preferred lower limit of Ni is 30%, and the more preferred upper limit of Ni is 36%.

[0028]

5 (5) Mo (molybdenum): 1-4.5%

Mo is combined with carbon to precipitate carbides in the cast iron matrix, thereby drastically increasing the yield strength of the matrix by precipitation strengthening in an entire range of temperatures used. Though Mo is a carbide-forming element, it has little tendency of hindering the spheroidization of graphite. Thus, the addition of Mo together with Sn and/or Sb improves the room-temperature elongation without decreasing the number of graphite particles precipitated and a graphite spheroidization ratio.

[0029]

Because Mo is an element having a small thermal expansion coefficient, it reduces the average thermal expansion coefficient of the cast iron up to around 1000°C, thereby decreasing a thermal strain in a high-temperature range, which is determined by the product of a thermal expansion coefficient and temperature, and thus lowering the resultant thermal stress. The synergistic effect of Mo with Si and Cr provide a dense and strong passive film of silicon oxide, chromium oxide, etc. formed on a surface, and suppresses surface oxidation, thereby improving the oxidation resistance of the cast iron. The synergistic effect of suppressing the thermal stress and improving the oxidation resistance provides the cast iron with a longer thermal fatigue life.

25 [0030]

Mo exceeding 4.5% decreases room-temperature elongation and machinability due to deteriorated spheroidization of graphite and increased precipitation of carbides. On the other hand, when Mo is less than 1%, the

matrix of the cast iron is not subjected to sufficient precipitation strengthening by the formation of carbides. Accordingly, Mo is 1-4.5%, preferably 2-4%.

[0031]

(6) $2\text{Sn} + \text{Sb}$: 0.001-0.5%

5 Both Sn and Sb increase the number of graphite particles while reducing their segregation, and increase a graphite spheroidization ratio to 75% or more, thereby suppressing Mo from reducing ductility. Even if up to 6.5% of Si tending to reduce the ductility is contained, the addition of Sn and/or Sb provides the cast iron with enough room-temperature elongation
10 without reducing the number and spheroidization ratio of graphite particles. Sn and Sb also prevent the disappearance of graphite by internal oxidation, thereby providing the heat-resistant, austenitic spheroidal graphite cast iron with improved oxidation resistance. Though this mechanism is not necessarily clear, Sn and/or Sb are concentrated in boundaries between
15 graphite particles and a matrix on the matrix side, suppressing C from diffusing from graphite to the matrix, and suppressing oxygen entering into the matrix from reacting with graphite.

[0032]

Because Sb is 2 times as effective as Sn, the amounts of Sn and/or Sb
20 are expressed by $(2\text{Sn} + \text{Sb})$. When $(2\text{Sn} + \text{Sb})$ exceeds 0.5%, flake-shaped abnormal graphite is formed in eutectic cell boundaries, and cementite is formed in the matrix structure, resulting in reduced toughness and room-temperature elongation, while accelerating internal oxidation. On the other hand, when Sn and/or Sb are less than 0.001%, the above effects are not
25 obtained. Accordingly, $(2\text{Sn} + \text{Sb})$ is 0.001-0.5%, preferably 0.005-0.5%, more preferably 0.01-0.4%.

[0033]

(7) N (nitrogen): 0.3% or less

N stabilizes an austenitic structure and improves the high-temperature yield strength of the matrix. However, when N exceeds 0.3%, the amount of nitrides precipitated increases, and the spheroidization of graphite is hindered, resulting in decreased toughness, and more generation of gas defects such as pinholes, etc. during casting. Accordingly, N is 0.3% or less. Though N is an element inevitably contained in the austenitic spheroidal graphite cast iron usually in an amount of about 0.002-0.006%, the predetermined amount of N is added when high yield strength is needed at high temperatures. N is preferably 0.01-0.3%, more preferably 0.03-0.2%.

10 To add N, for instance, lime nitrogen or chromium nitride (Cr_3N) is added to the melt, or a nitrogen gas is blown into the melt.

[0034]

(8) Graphite-spheroidizing elements: 0.1% or less

To crystallize spheroidal graphite in an as-cast state to improve properties such as room-temperature elongation, high-temperature yield strength, etc., a graphite-spheroidizing element such as Mg or Ca in pure Mg, Fe-Si-Mg alloys, etc. is added in an amount of 0.1% or less. The amount of Mg added is preferably 0.02-0.08%.

[0035]

20 (9) Other elements

The heat-resistant, austenitic spheroidal graphite cast iron of the present invention may contain Mn and Cu in ranges not deteriorating room-temperature elongation, oxidation resistance, high-temperature yield strength and thermal fatigue life. Mn is an element necessary for stabilizing the austenitic structure, but more than 1.5% of Mn would deteriorate the toughness and heat resistance of the cast iron, be likely to generate gas defects such as blow holes, etc. Cu is, like Ni, dissolved in the matrix to stabilize the austenitic structure, making crystal grains in the matrix structure finer,

thereby contributing to the improvement of high-temperature yield strength, and improving oxidation resistance and corrosion resistance. However, more than 3% of Cu hinders the spheroidization of graphite, and reduces ductility by the formation of carbide. Accordingly, when Mn and Cu are added, Mn is preferably 1.5% or less, and Cu is preferably 3% or less.

[0036]

Inevitable impurities are P and S. P is not only harmful to the spheroidization of graphite, but also precipitated in grain boundaries, deteriorating oxidation resistance and room-temperature elongation.

10 Accordingly, P is preferably 0.08% or less. Because S is also harmful to spheroidization of graphite, S is preferably 0.025% or less.

[0037]

[2] Properties of heat-resistant, austenitic spheroidal graphite cast iron

Because the heat-resistant, austenitic spheroidal graphite cast iron of the present invention is used for exhaust equipment members for automobile engines, which are exposed to an exhaust gas at 900°C or higher, particularly around 1000°C, it should have enough room-temperature elongation, oxidation resistance and high-temperature yield strength. Accordingly, it preferably meets the conditions that its room-temperature elongation is 2% or more, that its weight loss by oxidation is 30 mg/cm² or less when it is kept in the air at 950°C for 200 hours, and that its 0.2-% yield strength is 55 N/mm² or more in the air at 950°C. To meet such conditions, particularly the high-temperature yield strength should be improved while keeping the room-temperature elongation. Thus, the heat-resistant, austenitic spheroidal graphite cast iron preferably has 75% or more of a graphite spheroidization ratio.

[0038]

When the austenitic spheroidal graphite cast iron has less than 2.0%

of room-temperature elongation, it is likely subjected to cracking by vibration and shock applied during the production of exhaust equipment members, their assembling to engines, at the time of start and during operation of automobile engines, etc. As a practically sufficient level, the room-temperature elongation is preferably 2% or more.

[0039]

The heat-resistant, austenitic spheroidal graphite cast iron used for exhaust equipment members for automobile engines is required to have enough room-temperature elongation and heat resistance (oxidation resistance and high-temperature yield strength). The weight loss by oxidation in the air at 950°C and 0.2-% yield strength are indices expressing the level of heat resistance. Smaller weight loss by oxidation and higher high-temperature yield strength lead to better heat resistance.

[0040]

The exhaust equipment members are exposed to sulfur oxides, nitrogen oxides, etc. contained in exhaust gases discharged from engines. When oxidation occurs, oxide films are first formed on a surface, from which microcracks are generated, and the oxidation of microcracks accelerates cracking. By this repetition, cracking propagates deep inside the members.

With weight loss by oxidation exceeding 30 mg/cm² when kept in the air at 950°C for 200 hours, lots of oxide films, from which cracking occurs, are formed on a surface, resulting in insufficient oxidation resistance. Accordingly, the weight loss by oxidation is preferably 30 mg/cm² or less.

[0041]

With 0.2-% yield strength of less than 55 N/mm² at 950°C in the air, it is difficult to provide the constrained exhaust equipment members with enough strength to resist a compression stress at high temperatures. Accordingly, the 0.2-% yield strength at 950°C in the air is 55 N/mm² or more,

preferably 60 N/mm^2 or more.

[0042]

The exhaust equipment members should have a long thermal fatigue life to the repetition of operation (heating) and stop (cooling) of engines.

- 5 Specifically, in a thermal fatigue test, in which heating and cooling are repeated at the highest temperature of 950°C , a temperature amplitude of 800°C and a constraint ratio of 0.5, the number of cycles (thermal fatigue life) until fracture occurs by cracking is desirably 400 or more. The thermal fatigue life under this condition is an index expressing how high the heat
- 10 resistance is. When the thermal fatigue life is less than 400 cycles, exhaust equipment members exposed to an exhaust gas at 900°C or higher, particularly around 1000°C do not have a sufficient thermal fatigue life.

[0043]

- The exhaust equipment members are cracked due to a thermal stress
- 15 generated by the repetition of expansion during heating and shrinkage during cooling. To suppress the thermal stress, the exhaust equipment members preferably have the above room-temperature elongation, oxidation resistance and high-temperature yield strength, and a small average thermal expansion coefficient between room temperature and a high-temperature region. When
- 20 thermal strain in a high-temperature range, which is determined by the product of a thermal expansion coefficient and a temperature, is reduced, resulting in less thermal stress generated, the exhaust equipment members are provided with an improved thermal fatigue life. To obtain sufficient increase in the thermal fatigue life, the average thermal expansion coefficient in a
- 25 range from room temperature to 1000°C is preferably $18 \times 10^{-6}/^\circ\text{C}$ or less.

[0044]

The present invention will be explained in more detail referring to

Examples below without intention of restricting the present invention thereto.

[0045]

Examples 1-17, and Comparative Examples 1-13

Each heat-resistant, austenitic spheroidal graphite cast iron having a
5 chemical composition (% by weight) shown in Table 1 was melted in a
100-kg high-frequency furnace in the air, tapped from the furnace at 1450°C
or higher, and poured into a mold at 1300°C or higher to cast a block-shaped
sample of 25 mm x 25 mm x 165 mm. The samples of Examples 1-17 are
within the range of the present invention, and the samples of Comparative
10 Examples 1-13 are outside the range of the present invention. The samples
of Comparative Examples 1-3 contained less than 1% of Mo, the samples of
Comparative Examples 4-9 and 11 contained no Sn and Sb at all, the sample
of Comparative Example 10 contained more than 4.5% of Mo, the sample of
Comparative Example 12 contained more than 0.5% of (2Sn + Sb), and the
15 sample of Comparative Example 13 contained more than 0.3% of N. The
sample of Comparative Example 4 corresponds to NI-RESIST D5S (JIS G
5510, JIS-FCDA NiSiCr 35 5 2) containing no Mo, Sn and Sb at all.

[0046]

Table 1

| No. | Chemical Composition (% by weight) | | | | | | | | | |
|-------------|------------------------------------|------|------|------|------|--------|--------|--------|--------|-------|
| | C | Si | Cr | Ni | Mo | Sn | Sb | 2Sn+Sb | N | Mg |
| Example 1 | 1.97 | 3.75 | 1.70 | 28.5 | 1.18 | - | 0.0012 | 0.0012 | 0.0065 | 0.072 |
| Example 2 | 2.01 | 3.94 | 1.61 | 26.9 | 1.23 | 0.0007 | - | 0.0014 | 0.0053 | 0.066 |
| Example 3 | 2.05 | 4.52 | 1.78 | 30.4 | 2.01 | - | 0.0052 | 0.0052 | 0.0107 | 0.063 |
| Example 4 | 2.11 | 4.56 | 1.65 | 31.3 | 2.04 | 0.0054 | - | 0.0108 | 0.0123 | 0.071 |
| Example 5 | 1.87 | 4.85 | 1.72 | 32.6 | 2.21 | - | 0.0201 | 0.0201 | 0.0507 | 0.069 |
| Example 6 | 1.94 | 5.13 | 1.68 | 31.5 | 3.05 | 0.0109 | - | 0.0218 | 0.0713 | 0.075 |
| Example 7 | 2.04 | 4.54 | 1.72 | 34.1 | 1.41 | 0.0067 | 0.0078 | 0.0212 | 0.0042 | 0.071 |
| Example 8 | 2.03 | 4.47 | 1.67 | 34.1 | 1.40 | 0.0005 | 0.0005 | 0.0015 | 0.0104 | 0.077 |
| Example 9 | 2.03 | 4.98 | 1.65 | 35.3 | 1.82 | 0.0052 | 0.0104 | 0.0208 | 0.0153 | 0.078 |
| Example 10 | 2.08 | 5.03 | 1.74 | 34.6 | 2.03 | 0.0102 | 0.0098 | 0.0302 | 0.0268 | 0.076 |
| Example 11 | 2.03 | 5.01 | 1.61 | 35.1 | 2.15 | 0.0082 | 0.0097 | 0.0261 | 0.0302 | 0.071 |
| Example 12 | 2.02 | 5.03 | 1.74 | 34.7 | 2.86 | 0.0095 | 0.0104 | 0.0294 | 0.0511 | 0.072 |
| Example 13 | 2.08 | 5.05 | 1.58 | 34.2 | 3.47 | 0.0126 | 0.0146 | 0.0398 | 0.0456 | 0.078 |
| Example 14 | 1.98 | 5.00 | 1.61 | 35.7 | 3.96 | 0.0064 | 0.0213 | 0.0341 | 0.1993 | 0.077 |
| Example 15 | 2.08 | 4.95 | 1.60 | 34.4 | 4.23 | 0.0003 | 0.0005 | 0.0011 | 0.2897 | 0.079 |
| Example 16 | 2.03 | 5.01 | 1.69 | 35.9 | 4.36 | 0.2053 | 0.0678 | 0.4784 | 0.1872 | 0.075 |
| Example 17 | 1.99 | 4.99 | 1.64 | 35.5 | 4.49 | 0.2014 | 0.0897 | 0.4925 | 0.2974 | 0.072 |
| Com. Ex. 1 | 2.18 | 4.89 | 1.78 | 32.7 | 0.12 | 0.0004 | 0.0006 | 0.0014 | 0.0026 | 0.070 |
| Com. Ex. 2 | 2.15 | 4.86 | 1.77 | 32.6 | 0.18 | - | 0.0335 | 0.0335 | 0.0061 | 0.068 |
| Com. Ex. 3 | 2.16 | 4.88 | 1.72 | 33.1 | 0.23 | 0.0122 | - | 0.0244 | 0.0058 | 0.073 |
| Com. Ex. 4 | 2.16 | 5.01 | 1.72 | 34.2 | - | - | - | - | 0.0025 | 0.062 |
| Com. Ex. 5 | 2.06 | 4.99 | 1.72 | 34.1 | 1.46 | - | - | - | 0.0048 | 0.068 |
| Com. Ex. 6 | 2.05 | 4.97 | 1.68 | 34.4 | 1.96 | - | - | - | 0.0034 | 0.071 |
| Com. Ex. 7 | 2.05 | 4.98 | 1.70 | 34.7 | 2.88 | - | - | - | 0.0042 | 0.076 |
| Com. Ex. 8 | 2.05 | 4.96 | 1.64 | 34.6 | 4.02 | - | - | - | 0.0027 | 0.075 |
| Com. Ex. 9 | 2.05 | 5.04 | 1.63 | 34.2 | 4.87 | - | - | - | 0.0033 | 0.071 |
| Com. Ex. 10 | 2.07 | 4.98 | 1.66 | 34.9 | 4.73 | 0.2185 | 0.0603 | 0.4973 | 0.0041 | 0.070 |
| Com. Ex. 11 | 2.08 | 5.04 | 1.67 | 34.0 | 2.82 | - | - | - | 0.0498 | 0.078 |
| Com. Ex. 12 | 2.01 | 5.03 | 1.68 | 34.4 | 3.04 | 0.1984 | 0.2887 | 0.6855 | 0.0457 | 0.078 |
| Com. Ex. 13 | 2.05 | 5.05 | 1.74 | 34.1 | 2.94 | 0.0105 | 0.0126 | 0.0336 | 0.4185 | 0.078 |

[0047]

Each sample was subjected to the following evaluations.

(1) Room-temperature elongation

The samples of Examples 1-17 and Comparative Examples 1-13
5 were measured with respect to a graphite spheroidization ratio according to
JIS G5502 10.7.4. The results are shown in Table 2. Also, the
microstructures of the samples of Example 12 and Comparative Example 9
were microscopically observed. Fig. 1 is a photomicrograph (magnification:
100 times) showing the microstructure of the sample of Example 12, and Fig.
10 2 is a photomicrograph (magnification: 100 times) showing the microstructure
of the sample of Comparative Example 9.

[0048]

A flanged test piece having a gauge length of 50 mm and a diameter
of 10 mm in the gauge length was cut out of each sample, and set in an
15 electric-hydraulic servo, tensile test machine to measure room-temperature
elongation (%) at 25°C. Each sample was examined with respect to the
relation between a graphite spheroidization ratio and room-temperature
elongation. Fig. 3 shows the relation between the graphite spheroidization
ratio and the room-temperature elongation. Each sample was further
20 examined with respect to the relation between the amount of Mo and
room-temperature elongation. Fig. 4 shows the relation between the amount
of Mo and the room-temperature elongation.

[0049]

As is clear from Tables 1 and 2, all samples of Examples 1-17 had
25 graphite spheroidization ratios of 77-90%, meeting the condition of 75% or
more, and room-temperature elongations of 2.1-5.3%, meeting the condition
of 2% or more. On the other hand, the samples of Comparative Examples
5-9, to which only Mo was added, had graphite spheroidization ratios of

64-73%, less than 75%, and room-temperature elongations of 0.9-1.9%, less than 2.0%.

[0050]

As shown in Fig. 1, the microstructure of the sample of Example 12 had many graphite particles in a good spheroidal shape. Example 12 had as high a graphite spheroidization ratio as 84% and as high room-temperature elongation as 2.3%. As shown in Fig. 2, on the other hand, the sample of Comparative Example 9 containing as excessive Mo as 4.87% without Sn and/or Sb had a microstructure containing fewer graphite particles, many of which were not spheroidized. Comparative Example 9 had as low a graphite spheroidization ratio as 64% and as low room-temperature elongation as 0.9%.

[0051]

Fig. 3 indicates that the graphite spheroidization ratio should be 75% or more to obtain a practically sufficient room-temperature elongation (2% or more). If the austenitic spheroidal graphite cast iron had a microstructure having graphite particles deformed from a spheroidal shape to such an extent that the graphite spheroidization ratio becomes less than 75%, it would be close to gray cast iron (flake graphite cast iron) or vermicular cast iron, failing to obtain necessary strength and room-temperature elongation even though its matrix structure were strengthened.

[0052]

It is clear from Fig. 4 that though the higher Mo content leads to a lower room-temperature elongation, 2% or more of room-temperature elongation can be secured by containing Sn and/or Sb, if the Mo content is 4.5% or less. In the case of Comparative Example 10, in which the Mo content was as excessive as 4.73%, however, the room-temperature elongation was as low as 1.1% even though $(2\text{Sn} + \text{Sb})$ was close to 0.5%.

The sample of Comparative Example 12, in which (2Sn + Sb) was as excessive as 0.6855%, had low toughness, and as low room-temperature elongation as 1.3% even though the Mo content was 3.04%, within the range of the present invention.

5 [0053]

It is thus clear that the addition of 1-4.5% of Mo and 0.001-0.5% of Sn and/or Sb as (2Sn + Sb) can provide the heat-resistant, austenitic spheroidal graphite cast iron with practically sufficient 2% or more of room-temperature elongation without reducing the number of graphite particles and the graphite spheroidization ratio.

10 [0054]

(2) Oxidation resistance

Contemplating use for exhaust equipment members exposed to an exhaust gas at 900°C or higher, particularly around 1000°C, the oxidation resistance was evaluated at 950°C in the air. Specifically, a round rod test piece of 10 mm in diameter and 20 mm in length was cut out of each sample, kept at 950°C for 200 hours in the air, and subjected to shot blasting to remove oxide scales, thereby determining weight change (weight loss by oxidation) per a unit area before and after the oxidation test. Smaller weight loss means higher oxidation resistance. The results are shown in Table 2. Also, the relation between the Mo content and the weight loss by oxidation was investigated on each sample. The results are shown in Fig. 5.

20 [0055]

As is clear from Fig. 5, the weight loss by oxidation is minimum when the Mo content is about 3%, and sufficiently small weight loss by oxidation requires that the Mo content be 1-4.5%. In the samples of Examples 1-17, the weight loss by oxidation was 12.3 mg/cm² to 25.4 mg/cm², less than 30 mg/cm². On the other hand, the weight loss by oxidation was as

much as 32.5-59.0 mg/cm² in the samples of Comparative Examples 1-12. Particularly as compared with the sample of Comparative Example 4, a conventional austenitic spheroidal graphite cast iron (NI-RESIST D5S), which does not contain Mo, Sn and Sb, the samples of Examples 1-17 containing

5 Mo, Sn and Sb had much higher oxidation resistance.

[0056]

To investigate surface oxidation and the disappearance of internal graphite by oxidation, the microstructure of a sample after the oxidation test was microscopically observed. Fig. 6 is a photomicrograph (magnification:

10 400 times) showing the microstructure of the sample of Example 12 after the oxidation test, and Fig. 7 is a photomicrograph (magnification: 400 times) showing the microstructure of the sample of Comparative Example 4 containing no Mo, Sn and Sb after the oxidation test. The sample of Example 12 suffered little surface oxidation and was prevented from the

15 disappearance of graphite by oxidation, while the sample of Comparative Example 4 suffered severe surface oxidation, with oxide films intruding into voids generated by the disappearance of graphite by oxidation, part of internal graphite being disappeared or removed by oxidation.

[0057]

20 The comparison of weight loss by oxidation between the samples of Example 7 and Comparative Example 5 having substantially the same Mo content of about 1.4% with difference in the presence of Sn and Sb revealed that the weight loss by oxidation was 19.2 mg/cm² in Example 7, in which (2Sn + Sb) was 0.0212%, while it was 48.6 mg/cm² in Comparative Example

25 5 containing no Sn and Sb, as much as about 2.5 times that of Example 7. Likewise, the comparison of the samples of Example 12 and Comparative Example 11 having substantially the same Mo content of about 2.8% revealed that the weight loss by oxidation was 13.5 mg/cm² in the sample of Example

12, in which (2Sn + Sb) was 0.0294%, while it was 35.7 mg/cm² in the sample of Comparative Example 11 containing no Sn and Sb, as much as about 2.5 times that of Example 12.

[0058]

5 It is thus clear that not only Mo but also Sn and Sb contribute to improvement in the oxidation resistance. It is considered that such remarkable decrease in the weight loss by oxidation is caused by the synergistic effects of improving surface oxidation resistance by Mo and improving internal oxidation resistance by Sn and/or Sb. Accordingly, when
10 the Mo content was less than 1% as in Comparative Examples 1-3, the weight loss by oxidation was as much as 34.3-37.1 mg/cm² even when (2Sn + Sb) was 0.0014-0.0335%, within the range of the present invention. Also, when (2Sn + Sb) was 0.6855%, exceeding the upper limit of 0.5%, the weight loss by oxidation drastically increased to 55.6 mg/cm² as in Comparative Example
15 12, even if the Mo content was within the range of the present invention. This is due to the fact that excess Sn and Sb rather accelerate internal oxidation.

[0059]

It is thus clear that to improve oxidation resistance such that the
20 weight loss by oxidation was 30 mg/cm² or less when kept at 950°C for 200 hours in the air, the Mo content should be 1-4.5%, and (2Sn + Sb) should be 0.001-0.5%. Particularly in Examples 3-6 and 10-14 the weight loss by oxidation was less than 15 mg/cm², and to obtain such low weight loss by oxidation, the Mo content is preferably 2-4%.

25 [0060]

(3) High-temperature yield strength

The high-temperature yield strength of each sample was determined by cutting each sample to form a flanged test piece having a gauge length of

50 mm and a diameter of 10 mm in the gauge length, which was set in an electric-hydraulic servo thermal-fatigue-measuring machine to measure 0.2-% yield strength at 950°C in the air. The results are shown in Table 2. Fig. 8 shows the relation between the Mo content and the high-temperature yield strength.

[0061]

It is clear from Fig. 8 that increase in the Mo content leads to increase in the high-temperature yield strength, and that the samples of Examples 1-17 are superior to those of Comparative Examples 1-13 in high-temperature yield strength. Particularly, the sample of Comparative Example 4 containing no Mo, Sn and Sb had high-temperature yield strength of 51.0 N/mm², while those of Examples 1-17 had as high high-temperature yield strength as 56.2-71.6 N/mm². It is thus clear that 1-4.5% of Mo should be contained to have a 0.2-% yield strength of 55 N/mm² or more at 950°C in the air. Incidentally, any of Comparative Examples 5-13 had high-temperature yield strength of more than 55 N/mm² and insufficient room-temperature elongation of less than 2.0%, most of these samples having weight loss by oxidation exceeding 30 mg/cm².

[0062]

Examples 7 and 8 and Comparative Example 5 containing the same amount (about 1.4%) of Mo were compared with respect to high-temperature yield strength, as samples having substantially the same Mo content and different N contents. It was thus found that the samples of Example 7 and Comparative Example 5 containing N in amounts of 0.0042% and 0.0048% (both inevitable levels), respectively, had high-temperature yield strength of about 57 N/mm², while the sample of Example 8 intentionally containing 0.0104% of N had high-temperature yield strength of 64.4N/mm², about 7 N/mm² higher. Comparison between Example 10 and Comparative Example

6, between Example 12 and Comparative Example 7, and between Example 14 and Comparative Example 8, respectively containing substantially the same amount of Mo, revealed that the samples of Comparative Examples 6, 7, 8 containing N in inevitable levels had high-temperature yield strength of about 58 N/mm², 62 N/mm² and 62 N/mm², respectively, while the samples of Examples 10, 12, 14 intentionally containing 0.01% or more of N had high-temperature yield strength of about 67 N/mm², 71 N/mm² and 72 N/mm², respectively, about 9-10 N/mm² higher.

[0063]

10 It is thus clear that Mo and N largely contribute to improvement in the high-temperature yield strength. This is due to the fact that N provides a stabilized austenitic structure and a strengthened matrix, thereby improving the high-temperature yield strength. It is clear that when as high high-temperature yield strength as 60 N/mm² or more is required, it is effective to add N in an amount exceeding its inevitable level. However, when about 0.42% of N exceeding the upper limit is contained as in Comparative Example 13, the room-temperature elongation becomes as low as 0.8%, and the thermal fatigue life is drastically shortened, though the high-temperature yield strength is improved. This is due to the fact that excess N increases the amount of nitrides precipitated and deteriorates a graphite spheroidization ratio, resulting in decreased toughness, and also generates gas defects such as pinholes, etc. during casting.

[0064]

(4) Thermal fatigue life

25 A round rod test piece having a gauge length of 20 mm and a diameter of 10 mm in the gauge length under was cut out of each sample, and set in an electric-hydraulic servo thermal-fatigue-measuring machine. A cycle of heating and cooling was repeated under the conditions that a ratio of

mechanically constraining elongation and shrinkage was 0.5, that the lower limit temperature was 150°C, that the highest temperatures were 750°C, 800°C and 950°C (temperature amplitudes of 600°C, 650°C and 800°C), respectively, and that one cycle was 7 minutes, to cause thermal fatigue fracture by cracking, thereby measuring the number of cycles until fracture occurred to determine the thermal fatigue life.

[0065]

The constraint ratio is expressed by (free thermal elongation - thermal elongation under mechanical constraint) / (free thermal elongation). For instance, the constraint ratio of 1.0 means that a test piece is mechanically constrained such that it is not elongated at all when heated, for instance, from 150°C to 950°C. Also, the constraint ratio of 0.5 means that a test piece is mechanically constrained such that it is elongated by 1 mm, for instance, when it is elongated by 2 mm in the case of free thermal elongation. Usually, the exhaust equipment members such as turbine housings, exhaust manifolds, catalyst cases, etc. are not constrained at a constraint ratio of 1.0, but assembled at a constraint ratio of about 0.25-0.5, which permits elongation to some extent by heating and cooling. Accordingly, the thermal fatigue life was evaluated at a constraint ratio of 0.5, which is close to an actual use condition. The results are shown in Table 2.

[0066]

Fig. 9 shows the relation between the Mo content and a thermal fatigue life at a temperature of 950°C and at a constraint ratio of 0.5. Fig. 9 indicates that when the Mo content was about 3%, the thermal fatigue life was longest, and that when the Mo content was within a range of 1-4.5% (Examples 1-17), the thermal fatigue life was 400 cycles or more. On the other hand, any samples of Comparative Examples 1-13 had thermal fatigue lives of less than 400 cycles. Thus, the samples of Examples 1-17 have

longer thermal fatigue lives than those of Comparative Examples 1-13. This is presumably due to the synergistic effects of the inclusion of Mo for suppressing thermal stress at high temperatures, and the inclusion of Sn and/or Sb for providing enough ductility in a range from room temperature to a high temperature and improving oxidation resistance. In Comparative Example 9 containing as much Mo as more than 4.87%, the spheroidization of graphite was deteriorated, and the thermal fatigue life was as extremely short as 195 cycles. In Comparative Example 12 containing too much Sn and Sb and Comparative Example 13 containing too much N, too, the thermal fatigue life was as short as 291 cycles and 122 cycles, respectively. This indicates that if any one of Mo, Sn, Sb and N were excessive, the heat-resistant, austenitic spheroidal graphite cast iron would have a short thermal fatigue life.

[0067]

It is thus clear that the Mo content should be 1-4.5%, and (2Sn + Sb) should be 0.001-0.5%, to obtain a thermal fatigue life of 400 cycles or more in a thermal fatigue test of heating and cooling at the highest temperature of 950°C, a temperature amplitude of 800°C and a constraint ratio of 0.5.

[0068]

(5) Average thermal expansion coefficient

A round rod test piece of 5 mm in diameter and 20 mm in length was cut out of each sample, set in a thermomechanical analyzer (TAS200 available from Rigaku Corporation), heated from room temperature to 1000°C at a temperature-elevating speed of 10°C/minute to measure the expansion of the test piece every 100°C to determine an average thermal expansion coefficient between room temperature and 1000°C. The results are shown in Table 2. Table 3 shows the measured thermal expansion coefficients of Example 12 and Comparative Example 4 in each temperature range.

[0069]

Table 2

| No. | Graphite Spheroidization Ratio (%) | Elongation at Room Temperature (%) | Weight Loss by Oxidation (mg/cm ²) at | High-Temperature Yield Strength (N/mm ²) at |
|-------------|---|---|---|---|
| | | | 950°C | 950°C |
| Example 1 | 88 | 4.8 | 25.4 | 58.4 |
| Example 2 | 86 | 4.2 | 23.1 | 56.2 |
| Example 3 | 84 | 3.2 | 14.4 | 63.7 |
| Example 4 | 82 | 2.8 | 13.9 | 67.5 |
| Example 5 | 82 | 2.4 | 12.5 | 68.6 |
| Example 6 | 79 | 2.5 | 12.6 | 70.7 |
| Example 7 | 90 | 5.3 | 19.2 | 57.2 |
| Example 8 | 85 | 2.9 | 22.4 | 64.4 |
| Example 9 | 86 | 3.3 | 16.8 | 65.3 |
| Example 10 | 84 | 3.0 | 12.4 | 66.5 |
| Example 11 | 83 | 2.4 | 12.6 | 69.8 |
| Example 12 | 84 | 2.3 | 13.5 | 70.6 |
| Example 13 | 81 | 2.8 | 12.3 | 68.6 |
| Example 14 | 80 | 2.2 | 12.7 | 71.6 |
| Example 15 | 79 | 2.1 | 16.1 | 71.3 |
| Example 16 | 78 | 2.2 | 16.8 | 69.8 |
| Example 17 | 77 | 2.1 | 18.7 | 70.6 |
| Com. Ex. 1 | 92 | 8.7 | 35.4 | 55.2 |
| Com. Ex. 2 | 94 | 8.9 | 34.3 | 56.4 |
| Com. Ex. 3 | 91 | 8.4 | 37.1 | 56.0 |
| Com. Ex. 4 | 86 | 11.5 | 59.0 | 51.0 |
| Com. Ex. 5 | 73 | 1.9 | 48.6 | 57.0 |
| Com. Ex. 6 | 72 | 1.7 | 41.5 | 58.1 |
| Com. Ex. 7 | 69 | 1.6 | 39.8 | 61.9 |
| Com. Ex. 8 | 66 | 1.4 | 37.2 | 62.3 |
| Com. Ex. 9 | 64 | 0.9 | 47.4 | 64.3 |
| Com. Ex. 10 | 68 | 1.1 | 32.5 | 63.6 |
| Com. Ex. 11 | 70 | 1.6 | 35.7 | 68.3 |
| Com. Ex. 12 | 65 | 1.3 | 55.6 | 58.8 |
| Com. Ex. 13 | 66 | 0.8 | 21.4 | 69.9 |

Table 2 (Continued)

| No. | Thermal Fatigue Life (Cycles) at | | | Average Thermal Expansion Coefficient Between Room Temperature and 1000°C ($\times 10^{-6}/^{\circ}\text{C}$) |
|-------------|-------------------------------------|-------|-------|--|
| | 750°C | 800°C | 950°C | |
| Example 1 | 623 | 531 | 428 | 17.9 |
| Example 2 | 637 | 519 | 416 | 17.8 |
| Example 3 | 705 | 611 | 457 | 17.6 |
| Example 4 | 886 | 742 | 525 | 17.5 |
| Example 5 | 894 | 757 | 582 | 17.4 |
| Example 6 | 952 | 823 | 675 | 17.4 |
| Example 7 | 734 | 632 | 477 | 17.8 |
| Example 8 | 655 | 541 | 412 | 17.6 |
| Example 9 | 743 | 594 | 497 | 17.5 |
| Example 10 | 939 | 834 | 632 | 17.4 |
| Example 11 | 753 | 660 | 461 | 17.5 |
| Example 12 | 971 | 889 | 712 | 17.4 |
| Example 13 | 908 | 775 | 581 | 17.4 |
| Example 14 | 962 | 842 | 661 | 17.3 |
| Example 15 | 711 | 593 | 476 | 16.9 |
| Example 16 | 984 | 861 | 697 | 16.8 |
| Example 17 | 634 | 548 | 426 | 16.8 |
| Com. Ex. 1 | 548 | 392 | 355 | 19.1 |
| Com. Ex. 2 | 560 | 409 | 362 | 18.9 |
| Com. Ex. 3 | 593 | 411 | 376 | 18.8 |
| Com. Ex. 4 | 455 | 374 | 298 | 19.5 |
| Com. Ex. 5 | 463 | 381 | 309 | 17.9 |
| Com. Ex. 6 | 547 | 472 | 342 | 17.7 |
| Com. Ex. 7 | 623 | 501 | 398 | 17.4 |
| Com. Ex. 8 | 552 | 482 | 376 | 17.3 |
| Com. Ex. 9 | 244 | 218 | 195 | 16.8 |
| Com. Ex. 10 | 536 | 502 | 372 | 16.9 |
| Com. Ex. 11 | 617 | 496 | 383 | 17.6 |
| Com. Ex. 12 | 498 | 395 | 291 | 17.5 |
| Com. Ex. 13 | 196 | 162 | 122 | 17.5 |

[0070]

Table 3

| Measured Temperature Range | Thermal Expansion Coefficient ($\times 10^{-6}/^{\circ}\text{C}$) | |
|-------------------------------|---|-----------------------|
| | Example 12 | Comparative Example 4 |
| RT ⁽¹⁾ to 300°C | 13.9 | 15.9 |
| RT to 400°C | 14.6 | 16.6 |
| RT to 500°C | 15.3 | 17.2 |
| RT to 600°C | 15.8 | 17.6 |
| RT to 700°C | 16.1 | 17.7 |
| RT to 800°C | 16.4 | 17.9 |
| RT to 900°C | 16.7 | 18.5 |
| RT to 1000°C | 17.4 | 19.5 |

Note: (1) Room temperature.

5 [0071]

Table 2 indicates that as the Mo content increases, the average thermal expansion coefficient decreases in a range from room temperature to 1000°C, and that when the Mo content exceeds 1%, the average thermal expansion coefficient becomes $18 \times 10^{-6}/^{\circ}\text{C}$ or less. Table 3 indicates that

10 Example 12 had a smaller thermal expansion coefficient by $1.5\text{-}2.1 \times 10^{-6}/^{\circ}\text{C}$ than that of Comparative Example 4 containing no Mo, Sn and Sb in every 100°C temperature range from room temperature to 300-1000°C. When the heat-resistant, austenitic spheroidal graphite cast iron is used for exhaust equipment members for automobile engines, its average thermal expansion

15 coefficient in a range from room temperature to 1000°C is desirably $18 \times 10^{-6}/^{\circ}\text{C}$ or less to suppress cracking due to thermal stress, requiring that the

Mo content be 1% or more.

[0072]

Fig. 10 shows exhaust equipment comprising an exhaust manifold 1, a turbocharger housing 2, and a catalyst case 4 as an example of the exhaust equipment members using the heat-resistant, austenitic spheroidal graphite cast iron of the present invention. In the exemplified exhaust equipment, an exhaust gas (indicated by the arrow A) discharged from an engine (not shown) is gathered in the exhaust manifold 1 to rotate a turbine (not shown) in the turbine housing 2 by the kinetic energy of the exhaust gas, and the air (shown by the arrow B) supplied by driving a compressor coaxially connected to this turbine is compressed to supply the compressed air to the engine as shown by the arrow C, thereby increasing the power of the engine. An exhaust gas discharged from the turbocharger housing 2 is supplied to the catalyst case 4 via a connection 3, and after harmful materials were removed by a catalyst in the catalyst case 4, it was discharged to the air via a muffler 5 as shown by the arrow D. An exhaust gas path passes through the exhaust manifold 1, the turbocharger housing 2, the connection 3 and the catalyst case 4. For instance, the exhaust gas path is as thick as 2.0-4.5 mm in the exhaust manifold 1, 2.5-5.5 mm in the turbocharger housing 2, 2.5-3.5 mm in the connection 3, and 2.0-2.5 mm in the catalyst case 4.

[0073]

Fig. 11 exemplifies a turbocharger housing 2, and Fig. 12 shows its A-A cross section. The turbocharger housing 2 comprises a spiral-shaped scroll portion 2a, whose hollow portion has a complicated shape having a cross section increasing from one end to the other. The turbocharger housing 2 is provided with a waist gate 2b for bypassing an excess exhaust gas for discharge by opening a valve (not shown). The waist gate 2b, through which a high-temperature exhaust gas flows, is particularly required

to have high oxidation resistance.

[0074]

The heat-resistant, austenitic spheroidal graphite cast iron having the composition of Example 12 was cast to form the exhaust manifold 1 and the
5 turbocharger housing 2, and then machined. The exhaust manifold 1 and the turbocharger housing 2 thus obtained were free from casting defects such as shrinkage cavities, misrun, gas defects, etc., and did not suffer insufficient cutting, etc. when machined.

[0075]

10 The connection 3 and the catalyst case 4 can also be produced by casting the heat-resistant, austenitic spheroidal graphite cast iron of the present invention. As long as molds can be formed and parted, the turbocharger housing 2 and the exhaust manifold 1 may be integrally cast, and the catalyst case 4 and the exhaust manifold 1 can integrally be cast when
15 there is not the turbocharger housing 2 therebetween.

[0076]

The exhaust manifold 1 and the turbocharger housing 2 formed by the heat-resistant, austenitic spheroidal graphite cast iron of Example 12 were connected to an exhaust simulator corresponding to high-performance,
20 2000-cc, straight, four-cylinder gasoline engine for a durability test. As a test condition, one heating-cooling cycle comprising heating for 10 minutes and cooling for 10 minutes were repeated 1000 times.

[0077]

The exhaust gas temperature at a full load was 980°C at an inlet of
25 the turbocharger housing 2. Under this condition, a surface temperature was about 900°C in a convergence portion of the exhaust manifold 1, and about 950°C on a seat 2c of the waist gate 2b of the turbocharger housing 2.

[0078]

Fig. 13 shows the appearance of the turbocharger housing 2 formed by the heat-resistant, austenitic spheroidal graphite cast iron of Example 12 near the waist gate 2b, after the durability test of 1000 cycles. As shown in Fig. 13, there was little oxidation in the waist gate 2b, through which a high-temperature exhaust gas passed, resulting in no thermal cracking, and no gas leakage due to thermal deformation. Thus, the turbocharger housing 2 had excellent durability and reliability. In the exhaust manifold 1, too, no thermal cracking and thermal deformation occurred after the durability test of 1000 cycles.

10 [0079]

Though vibration and shock were applied to the exhaust manifold 1 and the turbocharger housing 2 formed by the heat-resistant, austenitic spheroidal graphite cast iron of Example 12 at room temperature, during casting, machining, a durability test, etc., for instance, during the cutting of runners, finishing, transportation, cutting, assembling, etc., no cracking and fracture occurred. It was thus confirmed that they had sufficient ductility.

15 [0080]

For comparison, the turbocharger housing 2 formed by the heat-resistant, austenitic spheroidal graphite cast iron of Comparative Example 4 containing no Mo, Sn and Sb, which was connected to the exhaust manifold 1, was subjected to a durability test by an exhaust simulator under the same test conditions as in Examples. Fig. 14 shows the appearance of this turbocharger housing 2 near a waist gate 2b after the durability test. As shown in Fig. 14, rapid oxidation generated large cracks 2d in the waist gate 2b and deformation in the seat 2c by 540 heating-cooling cycles, about half of those in Example 12.

20

25

APPLICABILITY IN INDUSTRY

[0081]

As described above, the heat-resistant, austenitic spheroidal graphite cast iron of the present invention has sufficient room-temperature elongation and excellent heat resistance (oxidation resistance, high-temperature yield strength and thermal fatigue life). Though the heat-resistant, austenitic spheroidal graphite cast iron of the present invention contains expensive Ni, it has a lower melting point and better castability and machinability than those of the cast stainless steel, because it is based on C-rich cast iron. Accordingly, the heat-resistant, austenitic spheroidal graphite cast iron of the present invention can inexpensively produce thin, complicatedly shaped exhaust equipment members for automobile engines, such as exhaust manifolds, turbocharger housings, catalyst cases, etc., which are exposed to an exhaust gas at 900°C or higher, particularly around 1000°C, at a high yield without needing high casting techniques. Even if these exhaust equipment members are disposed in a severe temperature environment in the rear of engines, they exhibit sufficient heat resistance, making it possible to increase the initial performance of exhaust-gas-cleaning catalysts.

[0082]

Though the heat-resistant, austenitic spheroidal graphite cast iron of the present invention has been explained in cases where they are used for the exhaust equipment members for automobile engines, without intension of restriction, and it is also usable for parts for use in burning such as floors and carriers of incineration furnaces and heat treatment furnaces requiring enough room-temperature elongation and heat resistance, etc.

[0083]

The heat-resistant, austenitic spheroidal graphite cast iron of the present invention not only has enough room-temperature elongation, but also exhibits excellent heat resistance such as oxidation resistance,

high-temperature yield strength, thermal fatigue life, etc. when exposed to an exhaust gas at 900°C or higher, particularly near 1000°C, and can be produced inexpensively.